MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF

ARO 13249.1-C

AD A075371

## REPORT DOCUMENTATION PAGE

**READ INSTRUCTIONS BEFORE COMPLETING FORM**

| 1. REPORT NUMBER | 2. GOVT ACCESSION NO. | 3. RECIPIENT'S CATALOG NUMBER |
|---|---|---|
| | | |

| 4. TITLE *(and Subtitle)* | 5. TYPE OF REPORT & PERIOD COVERED |
|---|---|
| Mechanistic Studies of the Effect of Lead Salts on Double-Base Propellant Combustion. The Use of Model Systems. | Final Report 11-1-75 - 7-31-79 |
| | 6. PERFORMING ORG. REPORT NUMBER |

| 7. AUTHOR(s) | 8. CONTRACT OR GRANT NUMBER(s) |
|---|---|
| Joseph B. Levy        Edward R. Johnson | DAAG29-76-G-0087 |

| 9. PERFORMING ORGANIZATION NAME AND ADDRESS | 10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS |
|---|---|
| The Dept. of Chemistry The George Washington University Washington, D.C. 20052 | |

| 11. CONTROLLING OFFICE NAME AND ADDRESS | 12. REPORT DATE |
|---|---|
| U.S. Army Research Office Post Office Box 12211 Research Triangle Park, N.C. 27709 | Sep 79 |
| | 13. NUMBER OF PAGES |
| | 31 |

| 14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)* | 15. SECURITY CLASS. *(of this report)* |
|---|---|
| | Unclassified |
| | 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE |

**LEVEL**

16. DISTRIBUTION STATEMENT *(of this Report)*

Approved for public release; distribution unlimited

DDC RECEIVED OCT 19 1979 E

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

Final rept. 1 Nov 75-31 Jul 79,        ARO        13249.1-C

18. SUPPLEMENTARY NOTES

The findings in this report are not to be construed as an official Dept. of the Army position, unless so designated by other authorized documents.

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Lead salts; ballistic modifiers; nitroalkane decomposition; double-base propellants.

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

In this program the effects of lead oxide (PbO) on the thermal decomposition of n-propyl nitrate have been studied as a model for double-base propellants containing lead salts as ballistic modifiers. Only a small effect has been observed with n-propyl nitrate at the temperature range investigated, 157-186°C, but in the course of this study a very powerful catalysis by lead oxide of the thermal decomposition of nitroalkanes was discovered and investigated in some detail.

DD FORM 1473 EDITION OF 1 NOV 65 IS OBSOLETE        404 400

Lead oxide (PbO) brings about the thermal decomposition of nitroethane at 110-160°C at rates some $10^8$ those that would occur with no lead oxide present. The effect seems to be general for nitroalkanes having a carbonhydrogen bond alpha to the nitro group. Lead oxide is not transformed in the reaction and hence is assigned the role of a true catalyst. The reaction appears to occur on the lead oxide surface since pre-melted lead oxide shows no detectable catalysis. A variety of other metal oxides has been studied and only one, hydrated ferric ixide FeO(OH) has been shown to exert any effect. The results are discussed and an important role assigned to the aci-nitro form of the nitroalkane.

| Accession For | | |
|---|---|---|
| NTIS GRA&I | | |
| DDC TAB | | |
| Unannounced | | |
| Justification | | |
| By | | |
| Distribution/ | | |
| Availability Codes | | |
| Dist | Avail and/or | special |
| A | | |

FINAL REPORT


"Mechanistic Studies of the Effect
of Lead Salts on Double Base
Propellant Combustion. The Use of
Model Systems"


Grant No. DAAG-29-C-0087


The Department of Chemistry

The George Washington University

Edward R. Johnson

Joseph B. Levy
Principal Investigator

September 1979

Table of Contents

ABSTRACT

In this program the effects of lead oxide (PbO) on the thermal
decomposition of n-propyl nitrate have been studied as a model for
double-base propellants containing lead salts as ballistic modifiers.
Only a small effect has been observed with n-propyl nitrate at the tempera-
ture range investigated, 157-186°C, but in the course of this study a very
powerful catalysis by lead oxide of the thermal decomposition of nitroalkanes
was discovered and investigated in some detail.

Lead oxide (PbO) brings about the thermal decomposition of nitroethane
at 110-160°C at rates some $10^8$ those that would occur with no lead oxide
present. The effect seems to be general for nitroalkanes having a carbon-
hydrogen bond alpha to the nitro group. Lead oxide is not transformed in
the reaction and hence is assigned the role of a true catalyst. The reaction
appears to occur on the lead oxide surface since pre-melted lead oxide shows
no detectable catalysis. A variety of other metal oxides has been studied
and only one, hydrated ferric oxide $FeO(OH)$ has been shown to exert any effect.
The results are discussed and an important role assigned to the aci-nitro form
of the nitroalkane.

# INTRODUCTION

The effect of lead salts on the combustion of double-base propellants is an important one but one which, despite a number of studies, is not understood. Various theories (1,2,3) have been proposed but all are based on indirect evidence obtained in very complicated systems. In the present research the approach has been to study the interaction of lead oxide with a simple nitrate ester chosen to model the more complex double-base propellant systems.

The goal of this program has been to learn something about the basic chemistry of lead oxide and compounds related to double base propellants. In any basic research project it is important to investigate the unexpected result and in this project the unexpected result has been the substantial catalytic effect that lead oxide shows on the pyrolytic decomposition of nitroalkanes. Whether this effect is important to double-base propellant combustion, only time will tell. That it is important to learn about a powerful catalytic effect of lead oxide on compounds containing nitro groups seems beyond dispute. That is the area in which the most effort in this program was devoted and which is described herein.

# RESULTS

## Experiments with n-Propyl Nitrate

n-Propyl-nitrate (NPN) was chosen as the model compound for study and the first task undertaken was to establish some general procedure for examining the effect of solid additives. For the latter, lead oxide (PbO) was the compound of interest. Experiments were first done in a 500 ml glass bulb in which the pyrolysis of NPN was studied manometrically. Although data for the pyrolysis rate constant for this species could be found in this way it did

not prove convenient for studies of the effect of a solid additive.  A different procedure was then adopted, which with various modifications described in the Experimental Part, was used in the rest of this research.  This involved the use of a small vessel, generally a glass bulb of 10-20 cc capacity, which could be charged with the organic compound and the solid additive, evacuated, and heated at appropriate temperatures.  The vessel contents could then be removed either directly or by dissolving them in a suitable solvent and analyzed by a combination of gas chromatography and infrared or mass spectrometry.  In this way data for the pyrolysis of NPN by itself were obtained.  These are shown in Tables 1 and 2 and Fig. 1 and yield the expression for the pyrolysis rate constant

$$k = 10^{16.3} \exp - 40,200/RT \text{ sec} -1.$$

A few experiments were done with the above technique in which the effect of copper surfaces and of lead oxide on the rate of NPN pyrolysis were studied but only small effects were observed (4).  In the course of these experiments a new phenomenon was observed, the study of which has occupied the remainder of the research effort.

Although lead oxide showed no substantial effect on the kinetics of NPN pyrolysis, it showed a striking effect on the reaction stoichiometry.  Nitroethane, a principal product of the pyrolysis of NPN by itself, was absent as a product when lead oxide was present.  This was soon found to be caused by the rapid disappearance of nitrothane over lead oxide at temperatures where it (nitroethane) is stable in the absence of lead oxide.  This effect was so striking that the decision was made to investigate the pyrolysis of nitroalkanes and of nitroethane, in particular, in the presence of lead oxide.

## Experiments with Nitroalkane-Lead Oxide Mixtures

The first experiments of this sort were carried out at the temperatures where NPN pyrolysis had been studied, around 190°C. At this temperature only the reaction products could be studied, not the kinetics, since the reaction was over in a period of seconds. In the early part of these studies it was established that the reaction was of some generality for nitroalkanes. Nitromethane, 1- and 2-nitropropane showed reactivity similar to that for nitroethane. The only gaseous product identified at first for nitroethane was acetonitrile. Acetone was the principal product from 2-nitropropane, propionitrile was the principal product from 1-nitropropane and nitromethane yielded principally hydrogen cyanide. No reaction was observed for 2-methyl-2-nitropropane. Further studies were concentrated on nitroethane.

## Nitroethane-Lead Oxide

The temperature range of 120-160°C was found to be convenient for the study of the kinetics and stoichiometry of this system. The procedures used in these experiments varied with the goal of the particular experiment and are described in detail in the Experimental Part but for purposes of discussion, will be described in a general way here.

The reaction vessels were spherical Pyrex bulbs of about 15 ml capacity which were fitted with Fisher-Porter Teflon valves. For product composition studies the bulbs were charged with 0.1 ml of nitroalkane and 1.0 g. of lead oxide. They were then evacuated while chilled in liquid nitrogen, the valve closed and the bulb then warmed to room temperature and immersed in a constant-temperature salt bath for an appropriate time. The reaction was stopped by cooling the bulb and the contents examined by gas chromatography, infrared or mass spectroscopy. For kinetic measurements the procedure was

the same except that the nitroethane was sealed in a glass ampule and kept separate from the solid substrate until the reaction vessel was equilibrated thermally. The ampule was then broken using a magnetically-controlled plunger and the pressure-time curve plotted.

Before discussing the rate and product composition measurements it is useful to present some general observations about the reaction. The reaction was invariably marked by discoloration of the lead oxide. The formation of grey to black areas was clearly evident. Iodimetric analyses of the lead oxide at the end of a run showed no evidence of lead dioxide formation. If the lead oxide were melted in the reaction vessel and spread over the entire surface as a thin film (a procedure originally designed to maximize the surface area) and then cooled to reaction temperature, no reaction took place.

## Kinetic Studies of the Nitroethane-Lead Oxide System

A large number of experiments was carried out in which the pressure in the reaction vessel was recorded continuously as a function of time. All of these conformed to one pattern, cf. Fig. 2. There was an initial period, referred to hereafter as the induction period, followed by a period in which the pressure rose until it became constant. When the data were plotted as $\ln (P_{oo} - P_t)$ vs. time, the curve for the period following the induction period was linear. The temperature dependence of the data was characterized by the slopes of the linear portion of the curves and by the induction times. Experiments were carried out from $123^{o}C$ to $157^{o}C$. The data are shown in Table 3.

Two methods were used to determine the length of the induction period (I). The value determined by method 1, designated $I_1$, was simply the time during which the initial pressure remained essentially constant (cf Fig. 2). The value

determined by method 2, designated $I_2$, was determined using the log $(P_{oo}-P)$ vs. time plots. The two linear portions--the initial flat portion and later steep portion--were extended to give a point intersection which was taken as the induction period. Only the largest induction periods (at the lower reaction temperatures) show any significant differences in the two values.

Examination of the first-order rate constant values, Table 3, shows that the temperature variation is small. The trend toward higher values at the higher temperatures cannot be reliably separated from the variation within one temperature. (In view of the fact that, although the same weight of lead oxide was used each time, the exact configuration and surface present could not be controlled, the observed scatter is understandable.) The rate constants for the range 128-157°C can be encompassed in the value $k = .006 \pm .026$ sec$^{-1}$.

The induction periods on the other hand showed substantial temperature dependence. A plot log I vs. reciprocal absolute temperature, Fig. 3, is roughly linear. Interpretation of the slope in terms of E/R, where E is the activation energy and R the gas constant yields a value of about 41 kcal. mole$^{-1}$.

## Experiments on the Induction Period for the Nitroethane-Lead Oxide Reaction

The induction period has been defined by the fact that it is a period in which little or no pressure change is observed. We have established that very little chemical change in the gaseous substituents occurs either. Thus, a reaction sample was removed from a 140°C bath after fifteen seconds. From Fig. 3 the induction period at 140°C is about twenty-seven seconds. Analysis of the reaction vessel gaseous contents by gas chromatography showed that less than .01% of the nitroethane had been consumed. It may be pointed out that

once the reaction starts, it is largely over in a period of about ten seconds at this temperature.

We wondered whether the induction period involved some change in the catalyst surface that could persist from one filling with nitroethane to another, and devised experiments to investigate this.

In one experiment a reaction vessel was charged with 1.0g lead oxide, 50 microliters of nitroethane and a fragile sealed glass bulb containing 100 microliters of nitroethane. Reaction was carried out at 130°C for thirty minutes in the usual way and the flask evacuated. The usual discoloration of the catalyst (see above) was observed. The reaction vessel was then closed and the bulb containing the additional nitroethane was broken by means of a magnetically-controlled bar. An induction period in the range predicted for this temperature was observed. A similar experiment was performed which differed only in that the reaction products of the first charge of nitroethane were not removed. When the pressure levelled off, the glass bulb containing the additional nitro-ethane was broken. Again the usual induction period was observed.

## Experiments with α-Deuterated Nitroethane

Nitroethane with deuterium in the alpha position was prepared. Analysis by mass and nmr spectroscopy showed the material to be 75% dideutero and 25% monodeutero nitroethane. Table 3 contains data for kinetics experiments with this material at 153 and 154°C. The most striking difference is that the induction periods are two to three times those for ordinary nitroethane.

### Experiments with other Nitroalkanes

A few experiments were carried out with other nitroalkanes but studies in detail were not performed. An experiment with 2-nitropropane and
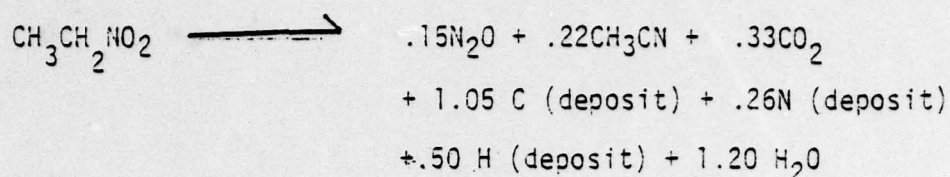
lead oxide at 140° C showed a much longer induction period than for nitro-
ethane (120 sec vs 15 sec) and a slope for the ln $(P_{oo} - P_t)$ vs t part of
the data of $5 \times 10^{-4}$ sec $^{-1}$, about two orders of magnitude less than that for
nitroethane. Experiments with 2-methyl-2-nitropropane and lead oxide in the
amounts used in the nitroethane experiments showed no reaction at all for
twenty-four hours at 180° C.

No kinetic experiments were done with nitromethane, 1-nitropropane and
1-nitrobutane, but in product composition experiments it was found that, for
the conditions used in the nitroethane experiments, these nitroalkanes were
completely decomposed after five minute heating periods at 190°C.

## The Reaction Products of the Nitroethane-Lead Oxide Reaction.

As the reaction proceeded a brown oily deposit began to form on the
lead oxide surface. At the end of a run the lead oxide was analyzed and
1.0 g. was found to contain 17.0 mg of carbon, 0.5 mg of hydrogen and 3.6 mg
of nitrogen. All of the above carbon however could not be assigned to the
brown deposit for treatment of the catalyst with acid released carbon dioxide
(identified by mass and infrared spectromemetry). The amount of carbon dioxide
found corresponded to 46% of the above carbon.

Analysis of the gaseous products showed the presence of nitrous oxide and
acetonitrile as the only major products. Water was qualitatively identified as
a product but no quantitative analyses were made. Small amounts (less than 1%
of the initial nitroethane) of nitrogen, acetaldoxime, ethylene, methane and
butene isomers were also identified by the combination of gas chromatography
and mass spectrometry. The analytical results are expressed by the following
equation

$$CH_3CH_2NO_2 \longrightarrow .15N_2O + .22CH_3CN + .33CO_2$$
$$+ 1.05 \text{ C (deposit)} + .26N \text{ (deposit)}$$
$$+.50 \text{ H (deposit)} + 1.20 \text{ H}_2O$$

In this equation the coefficient given for water is not based on analytical results but has been assigned to give a 100% mass balance for oxygen.

The following arguments can be cited as support for the coefficient assigned above for water. If it is assumed that the carbon dioxide arose from oxidation of the ethyl radical then one can propose that, for each carbon dioxide molecule formed, 2.5 molecules of water are produced. If one further makes the reasonable assumption that one molecule of water is formed for each molecule of nitrous oxide or acetonitrile then the total of these three sources is 1.20. The quantitative agreement with the figure cited above is probably fortuitous but the argument gives a logical basis for a figure of about this magnitude. The above expression accounts for about 70% of the total hydrogen. A few more percent can be assigned to the trace hydrocarbon products cited earlier.

Analyses of the Lead Oxide after a Run. The catalyst at the end of a run was also analyzed for lead dioxide (or any tretravalent lead) by treatment with potassium iodide, but none was ever found. Likewise dissolution of the catalyst at the end of a run in hydrochloric acid left no metallic lead residue. Blank experiments showed that as little as one milligram of lead would have been detected.

It thus appeared that lead oxide did function as a true catalyst in that it was neither oxidized or reduced and was chemically changed in the reaction only by absorption of carbon dioxide.

Experiments with Lead Dioxide.

Of the various things that could happen to lead oxide, oxidation to lead dioxide was one that could figure in a reaction mechanism. Since neither lead

dioxide nor lead appeared in the products it was of interest to see what happened with lead dioxide-nitroethane mixtures. These studies led us to look at the reactivity of lead dioxide with other compounds.

First a mixture containing lead oxide and lead dioxide in a 10:1 ratio was used in a typical run with nitroethane. Only lead oxide was found at the end. Hence the fact that lead dioxide was not found at the end of a nitroethane-lead oxide experiment did not rule it out as a transitory intermediate. Next the reaction of pure lead dioxide and nitroethane in amounts comparable to the nitroethane-lead oxide experiment were heated at an intermediate reaction temperature, 150° C. The reaction proceeded at a rate similar to that for lead oxide-nitroethane mixtures but the products were different. Nitrogen, carbon dioxide and, presumably, water were the products. No acetonitrile, a major product with lead oxide-nitroethane mixtures, was observed. Not all the lead dioxide reacted, but of the particles that did, lead oxide was found on the outer layer, red lead oxide $(Pb_3O_4)$ found inside this and lead dioxide found in the interior. These results prompted us to look at the reactions of lead dioxide with acetonitrile at 150°C. No comsumption of acetonitrile over a period of two hours was observed. This suggests that acetonitrile was never formed in the lead dioxide-nitroethane mixture and hence that there are significant differences in the way lead oxide and lead dioxide work.

In other experiments it was found that propionaldehyde, acetone, acetaldoxime and 2, 4-pentanedione all reacted with lead dioxide at 150°C. In the case of the last two of the above, the mixtures were observed to react at room temperature and to evolve enough heat to ignite the liquid either in air or in vacuum. On the other hand 2-methyl-2-nitropropane did not react with lead dioxide at 140°C nor did n-propyl nitrate.

## Experiments with other Metal Oxides.

Neither ferric acid ($Fe_2O_3$), stannous oxide, thorium dioxide ($ThO_2$) molybdenu[m]

trioxide ($MoO_3$) , barium oxide, cobaltous oxide or soda lime showed any effect

over thirty minutes at 150°C on nitroethane. Clearly basicity and multiple valen[ce]

states are not sufficient to show the effects that lead oxide does.

The only other material found to show reactivity similar to that of lead oxi[de]

was the iron oxide FeO(OH) (5) prepared as described in the Experimental Part.

This showed a reactivity very like that of lead oxide both in terms of reaction:

times and in the production of acetonitrile and acetaldoxime as products. This

phenomenon was discovered at the end of this study and it was not possible to

pursue it. The results of the experiments with lead dioxide and the other metal

oxides are collected in Table 4.


## DISCUSSION


Initially, when nitriles appeared to be a general reaction product, a tenta-

tive hypothesis was considered in which the lead oxide removed an oxygen from

the nitro group.

$$C_2H_5NO_2 + PbO \longrightarrow PbO_2 + C_2H_5NO$$

Isomerization of nitrosoalkanes to the corresponding oximes followed by dehydratio[n]

to nitriles is a well-established sequence. (6).

$$C_2H_5NO \longrightarrow CH_3CH = NOH \longrightarrow CH_3CN + H_2O$$
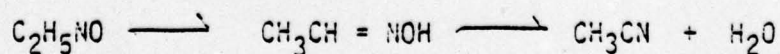
It was reasoned at that time that any lead dioxide formed would be reduced to the

lead oxide again. This appears to have been a correct assumption.

This hypothesis does not account for the stability of the tertiary nitro-alkane, 2-methyl-2-nitopropane. (It could be argued that the oxygen transfer itself is thermodynamically unfavorable and requires further reaction of the nitroso compound which cannot be shown by a tertiary nitroso compound and this is still a possibility  but does not seem likely). It likewise does not account for the formation of acetone from 2-nitropropane. This product was identified, not only by gas chromatography, but also by mass spectrometry when the reaction products were injected directly into the mass spectrometer. Formation of the ketone by hydrolysis of the corresponding oxime on the gas chromatographic column is thus ruled out. Finally the substantial increase in the induction period for $\alpha$, $\alpha$-dideutero nitroethane and for 2-nitropropane compared to nitroethane are not consistent with this idea.

That the principal products of nitroethane decomposition were acetonitrile and nitrous oxide suggests the conversion of the nitroalkanes to the corresponding aci-nitro isomer as the principal reaction path (7). Thus for nitroethane one can write

$$CH_3CH = N \begin{array}{c} O \\ OH \end{array} \quad + \quad H_2O \longrightarrow CH_3 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - N \begin{array}{c} OH \\ OH \end{array}$$

$$CH_3 \; \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}} - N \begin{array}{c} OH \\ OH \end{array} \longrightarrow H_2O + NOH + CH_3CHO$$

$$2 \; NOH \longrightarrow N_2O + H_2O$$

11

and

$$CH_3CH = N \overset{O}{\underset{OH}{<}} \quad + \; PbO \; \longrightarrow \; CH_3 \, CH = NOH \; + \; PbO_2$$

$$CH_3CH = NOH \; \longrightarrow \; CH_3CN \; + \; H_2O$$
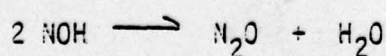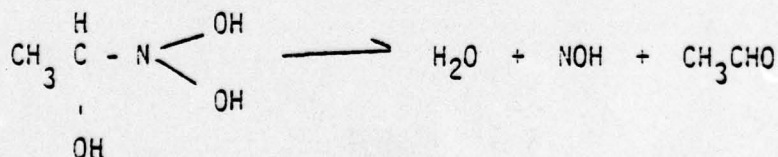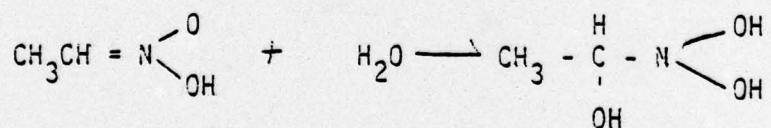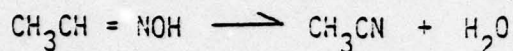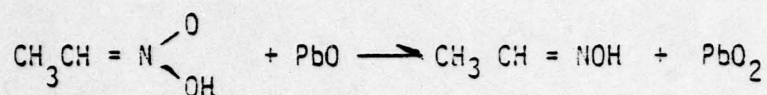
The evidence presented earlier makes it clear that lead dioxide, if formed in the reaction, would appear in the products as lead oxide. It also seems clear that acetaldehyde would not survive in this system but would be oxidized further.

The oily deposit clearly is some kind of polymerization product. Such products have been observed before in the pyrolysis of nitroalkanes.

A good deal of effort has been expended in this work on the induction period. From the point of view of the kinetics the results observed correspond to the following scheme.

$$C_2H_5NO_2 \; + \; surface \; \longrightarrow \; A.S \qquad\qquad (1)$$

$$C_2H_5NO_2 \; + \; A.S. \; \longrightarrow \; products \qquad\qquad (2)$$
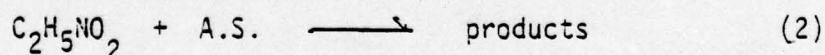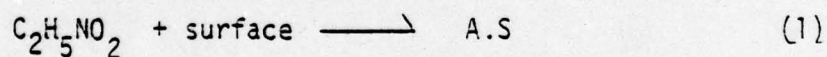
Here A.S. refers to active sites on the surface and the implication of expression (1) is the number of such sites is a function of the lead oxide and that the generation of these sites is what is going on in the induction period. The reaction kinetics then subsequent to the induction period would be given by

$$d \, (C_2H_5NO_2)/dt = k \, (C_2H_5NO_2) \qquad\qquad (3)$$

This is a first order expression in which the rate constant is given by

$$k = k_{(2)} \; (A.S)$$

Here $k_{(2)}$ is the rate constant for reaction (2) above and (A.S.), the concentration of active sites is a constant.

It can be noted that the formation of these active sites appears to involve the alpha hydrogen of the nitroalkane since the induction period did increase with alpha deuteration of nitroethane. The ten-fold increase in induction period in going (from nitroethane to 2-nitropropane corresponds quite closely to the decrease in the rate of proton removal from these molecules by hydroxide ion (nitroethane-2-nitropropane, rate constant ratio, approximately 230-300 : 19) (8)

## Why Does Lead Oxide Work ?

It seems most reasonable to attribute a dual role to lead oxide, i.e to suggest that it assists isomerization by proton transfer and that it reacts with the aci form by oxidation, reduction or both. The failure of more basic oxides and of other multivalent oxides to show perceptible catalytic effect shows that the requirements are quite subtle.

The only other oxide to show an effect, and indeed one very similar to that of lead oxide, was hydrated ferric oxide FeO(OH). Ordinary ferric oxide, $Fe_2O_3$ was ineffective. A reasonable route to isomerization can be written here
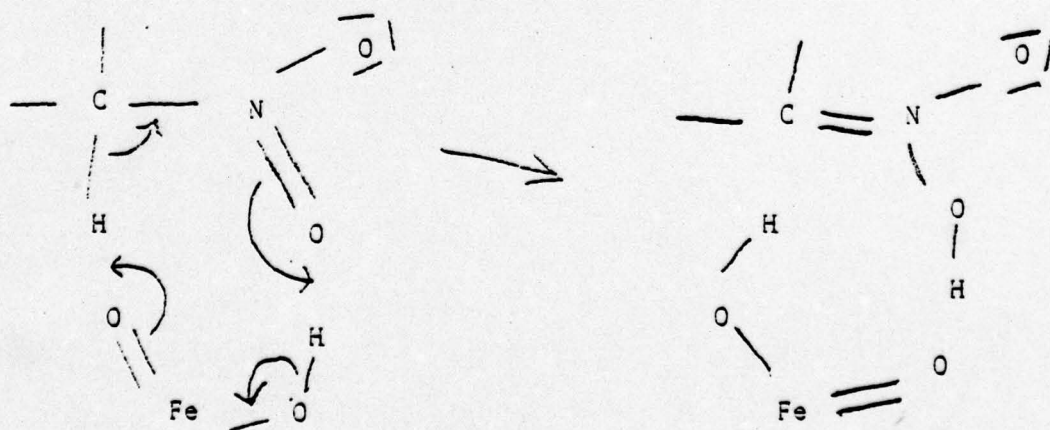
In the present study little effect was observed with n-propyl nitrate, the model for the double-base propellant , in the temperature range studied. It remains a point of importance as to whether a more substantial effect would be observed at higher temperatures, e.g. 250-300°C, which would be closer to the temperatures reported for the sufrace of burning propellants.

EXPERIMENTAL PART

## Materials

### The Nitrolkanes

The nitroalkanes were all obtained from Eastman Organic Chemicals Co.
and were reagent grade. Nitromethane, 1-and 2-nitropropane, 1-nitrobutane
and 2-methyl-2-nitropropane were all used without further treatment. Nitro-
ethane was distilled on a Nester-Faust 13" spinning band column. The fraction
distilling between 114.5° and 115.5° was collected. Gas chromatographic analysis
of this material indicated a purity greater than 99.5%. The identifiable impuri-
ties were nitromethane and 2-nitropropane.

### The Metal Oxides

Lead oxide (PbO, yellow) was either Coleman and Bell or Mallinkrodt reagent
grade. Lead dioxide (PbO$_2$), lead tetroxide (Pb$_3$O$_4$), ferric oxide (Fe$_2$O$_3$) thorium
dioxide (ThO$_2$), molybdenum trioxide (MoO$_3$), stannous oxide (SnO), barium oxide
(BaO) and soda lime were all commercial products, c.p or reagent grade and were
used without further treatment.

### Other Organic Compounds

Acetaldoxime was the Aldrich Chemical Co. product and was recrystallized
twice from water to remove trace amounts of acetonitrile. n-Propyl nitrate was
Eastman Organic Chemicals reagent grade and was distilled twice. Acetonitrile and
2,4-pentanedione were Eastman reagent grade and were used without further treat-
ment.

### Hydrated Ferric Oxide (FeO(OH))

A solution of ferric chloride hexahydrate (FeCl$_3$.6H$_2$O) (13.5 gms in 20cc H$_2$O)

was treated with 6 g of sodium hydroxide pellets. When the mixture had cooled, the resulting gel was collected on filter paper in a Buchner funnel. This gel was suspended in 50 ml ethanol for thirty minutes. The resulting solid was again collected on filter paper. The ethanol treatment was repeated. The resulting red brown solid was washed eith 25 ml of water and then dried in an oven at 110°.

## $\alpha, \alpha$-Dideuteronitroethane

The alpha dideuteration of nitroethane was achieved by treating the sodium salt with DCl. The salt, $Na(CH_3CHNO_2)$ was synthesized by slowing adding nitroethane to a solution of sodium methoxide. The salt was stored in the reaction flask under methanol and the amount necessary was removed before use. (Caution Na $CH_3CHNO_2$ is explosive). After collecting the salt on filter paper the white solid was washed with methanol but not allowed to dry. To 20 ml 99.7% $D_2O$ was slowly added 18 g of $Na(CH_3CHNO_2)$. The resulting solution was acidified by adding 24 ml of 20% DCL (in $D_2O$) dropwise. The nitroethane formed was extracted into ether and the ether layer was stored over molecular sieves. When a total of 54 g. of Na $(CH_3CH_3NO_2)$ (three batches) had been acidified the combined ether layers were distilled to collect the product $CH_3CHDNO_2$. This product was then slowly added to a solution of $NaOCH_3$ in $CH_3OD$. The resulting precipitate was collected on filter paper and washed with $CH_3OD$ (but not allowed to dry). This solid was treated analogously to Na $(CH_3CHNO_2)$. After workup 5 ml of nitroethane resulted. An NMR of this material indicated 25% $CH_3CHDNO_2$ and 75% $CH_3CD_2NO_2$. This isotopic distribution was also confirmed by mass spectrometry.

## Procedures

The procedures for experiments designed for product analyses and those

designed for reaction rate measurements were similar but had significant differences.

## Product Analysis Runs

Two general procedures were used for product analysis runs. A few were done directly in the gas chromatograph using a Valco zero dead volume valve that allowed the carrier gas stream to be diverted through a glass-stainless steel loop. The glass-to-metal joints were ground spherical joints with a Viton O-ring on the glass ball. The reaction loop was charged with lead oxide and nitroethane then cooled in liquid nitrogen and evacuated. The closed loop was placed in a 200°C oven for ten minutes. The valve wa then attached to the column in the gas chromatograph and the valve opened to allow the carrier gas to sweep the products on to the column. The analyses for condensible products were carried out using a small (15-20 ml) Pyrex flask equipped with a Fisher-Porter Teflon value and a side arm.
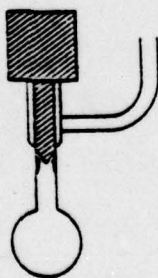


Typical conditions were: 0.75 ml nitroalkane, 1.0 g metal oxide, 150°C, for five minutes. The vessel was charged with the two reactants and immersed in liquid nitrogen. After the vessel had cooled the residual air was evacuated through the side arm. After evacuation the vessel was warmed to room temperature and then was immersed in a salt bath (53% $KNO_3$, 7% $NaNO_3$, and 40% $NaNO_2$).

After the desired time had elapsed the vessel was treated by one of the following methods.

a. The vessel was cooled in an ice bath for five minutes, the side arm filled with solvent (chloroform, methanol or ethyl ether) and the valve opened to draw the solvent into the vessel. The valve was closed and the mixture shaken for five minutes. Immediately prior to analysis the valve body was removed and the liquid decanted.

b. The end of the side arm was covered with a serum cap, the valve opened while the vessel was warm, and the gases (products and air) allowed to equilibrate five minutes before sampling.

c. The side arm was connected to a vacuum manifold and the products transferred to a small cold finger (3 cm x .3 cm).

d. The side arm of the reaction flask was connected directly to the gas inlet of a mass spectrometer the mass mass spectrum of the mixture was then recorded.

e. This procedure was developed for the analysis of carbon dioxide bound as lead carbonate. The reaction vessel was connected to a gas train designed for carbon dioxide absorption, described by Vogel (9). Phosphoric acid was added slowly and the gases evolved collected in the gas train. The system was flushed with air for five minutes and the mass gain measured. (A sample of authentic $PbCO_3$ showed this method was quantitative for $PbCO_3$).

f. For analysis of the oily organic material deposited on the lead oxide, the solid left at the end of a run was sent to Galbraith Laboratories (Knoxville, Tennessee) for analysis for carbon, hydrogen and nitrogen.

g. The side arm of the reaction vessel was connected to a vacuum manifold and the product mixture transferred to a 10 cm infrared gas cell.

## Analytical Methods

The products collected by the above methods were treated in the following manner.

The solution from (a.) was analyzed by gas chromatography. A seven foot by one-quarter inch column packed with 3% Carbowax 20m, or a six foot by one-quarter inch column packed with 10% trityl phosphate was used depending on which products were to be determined. The gas chromatography columns were in either a Perkin Elmer Model 270 mass spectrograph, a Finnigan Model 3300 mass spectrograph or a Perkin Elmer Sigma 3 gas chromatograph. Mass spectra were used for product identification while quantitative analyses were done on the gas chromatograph (Sigma 3), with methylene chloride as an internal standard. A majority of the quantitative work was done with the solutions from (c) and were done on the Sigma 3.

The gaseous mixtures from (b) were sampled with a Supelco gas-tight syringe and then injected onto a gas chromatograph column. A Porapak Q colum was used for separating nitrous oxide. A molecular sieve 4A column was used to separate nitrogen, oxygen and nitric oxide. The gases were injected onto a 0.19% picric acid on 80/100 mesh Carbopak C (Sulpelco) six foot column in the Sigma 3, equipped with flame ionization detector.

## Procedures for Rate Measurements.

A series of kinetic runs were done for these reactions. All kinetics runs were done by a continuous monitoring of the pressure. The apparatus for measuring the change in pressure was as follows: A Pyrex 25 (or 50) ml distilling flask was fitted with a 1/4" glass side arm and the metal oxide (typically 1.0 g) was placed in a pile on the bottom. A sealed fragile glass bulb containing 25-50 ml of reactant was added, a 7 g stir bar was placed above this and the top of the distilling flask was sealed in a flame.

The 1/4" tube was fitted to a stainless steel Swajelok Tee (using Nylon ferrules).
One end of the tee was connected to a stainless steel valve that went to the
vacuum system while the other end of the tee was attached to a pressure transducer
(Pace CD 25 ± 15 psi or P7D ± 5 psi). The transducer was connected to a Celesco
CD 25A transducer for dial readout. A permanent record was provided by attaching
a 10V strip chart recorder. (Maximum chart speed was 4 mm second$^{-1}$).
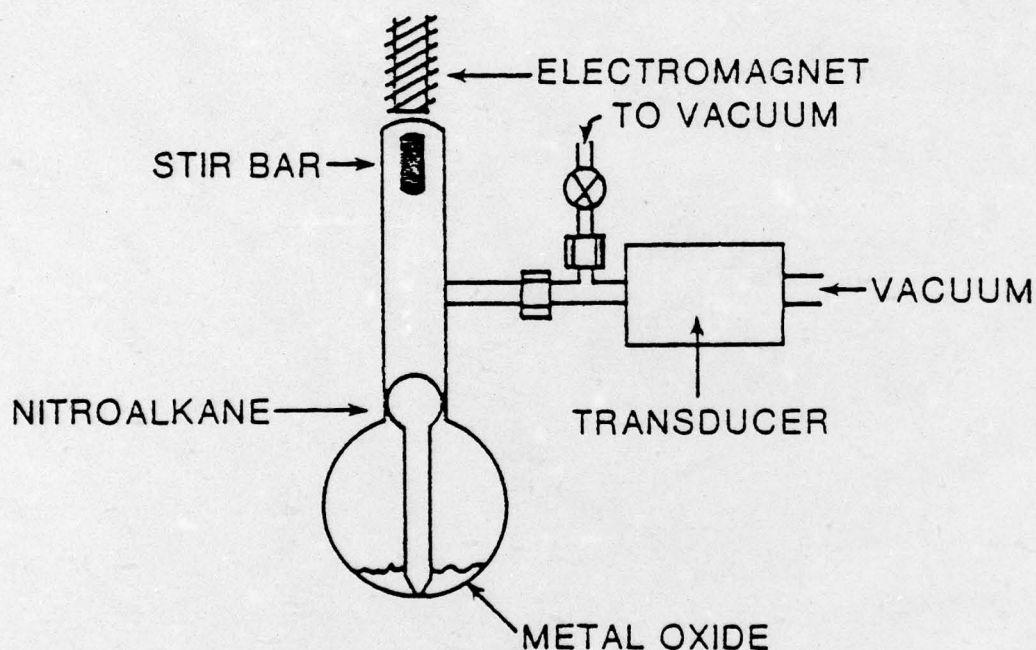


The entire apparatus was enclosed in an oven (±1°C). The apparatus was evacuated
while the system reached thermal equilibrium. After one hour the vacuum valve
was closed, the magnetic stir bar was raised to the top of the flask and the
system was allowed to equilibrate an additional one-half hour. At this time the
current to the electromagnet was reversed, the stir bar dropped shattering the bulb
and releasing the volatile reactant.

The pressure in the reaction vessel with no metal oxide present leveled off after 1.3 seconds (for runs done below 145° the vessel was heated to 145°C the cooled to reaction temperature). A plot of $\ln (P_\infty - P)$ vs time was made for all kinetic runs.

## Table 1

### Manometric Measurements of the First-Order

### Rate Constant for n-Propyl Nitrate Pyrolysis

| Ex Identification | Po (torr) | Temp | % Pressure Increase | First-Order Rate Constant ($sec^{-1}$) |
|---|---|---|---|---|
| p. 2 | 27.44 | 175 | 44.7 | $5.70 \times 10^{-4}$ |
| p. 2 | 25.45 | 175 | 51.6 | $5.40 \times 10^{-4}$ |
| p. 2 | 34.68 | 177 | 38.2 | $6.75 \times 10^{-4}$ |

## Table 2

### The Temperature Dependence of the

### Pyrolysis of n-Propyl Nitrate

| Temp (°C) | No. of experimental Points | $10^5 k$, ($sec^-$) |
|---|---|---|
| 157 | 6 | 12.1 |
| 167 | 6 | 23.1 |
| 177 | 5 | 58.3 |
| 186° | 8 | 141 |

## Table 3

### Reaction Rate Measurements for the
### Nitroethane-Lead Oxide System [a]

| Run[b] | t (°C) | Induction Times (sec.) $I_1$[c] | $I_2$[c] | $10^2k$ (sec$^{-1}$) |
|--------|--------|--------|--------|--------|
| A -6 | 157 | 13. | 16 | 8.16 |
| A-10 | 157 | 9.8 | 12.8 | 6.43 |
| A-5 | 156 | 11.5 | 16 | 8.71 |
| A-9 | 156 | 15.2 | 17.2 | 6.04 |
| A-4 | 153 | 17 | 17 | 4.92 |
| A-3 | 152 | 10 | 10 | 6.00 |
| A-15 | 152 | 8 | 8 | 7.27 |
| A-2 | 151 | 15 | 16.2 | 5.21 |
| A-1 | 150 | 11.5 | 11.5 | 5.35 |
| A-13 | 149 | 16.1 | 17.9 | 3.87 |
| B-2 | 148 | 16.5 | 17.5 | 6.66 |
| C-2 | 146 | 23.2 | 23.2 | 9.31 |
| B-4 | 143 | 22.5 | 22.5 | 6.97 |
| A-7 | 142 | 20.8 | 20.8 | 9.28 |
| A-13 | 138 | 42.5 | 50.5 | 4.35 |
| A-8 | 138 | 42.5 | 47.6 | 4.14 |
| A-14 | 128 | 100 | 138 | 4.79 |
| A-14 | 123 | 225 | 320 | .72 |
| | 110-115 | 7 3000 | | |
| D-1 | 153 | 28.7 | 28.7 | 3.36 |
| D-2 | 153 | 20 | 23.7 | 3.20 |
| D-3 | 154 | 25 | 30.6 | 4.11 |
| D-4 | 153 | 47 | 51.3 | 3.46 |

Table 3 (continued)

[a] Reaction temperature of air in the oven was constant to $\pm 1°C$.   $P_{\infty} - P$ was plotted in arbitory units from the chart, but $P_o$ for .1 ml nitroethane corresponded to $380 \pm 3$ torr.

[b] All runs designated A used 0.1 ml nitroethane; runs marked B used .05 ml nitro-ethane for pre-reaction and .05 ml nitroethane for the regular reaction thereafter. Runs designated D used 0.1 ml $\alpha, \alpha$-dideuteronitroethane (see text).

[c] See text for explanation of how these values were obtained.

## Table 4

### Summary of Reaction Products Found in Metal Oxide-Catalyzed Reactions with Nitroalkanes and Related Species

| Reaction Temperature | Organic Reactant | Oxide | Products observed | Analytical Method Used | | | |
|---|---|---|---|---|---|---|---|
| | | | | IR | GC | MS | GCMS |
| 180° | nitromethane | PbO | HCN | * | * | * | |
| " | nitromethane | | $N_2O$ | * | * | * | |
| " | | | $N_2$ | | * | * | |
| " | | | $H_2O$ | | * | * | |
| " | | | $CO_2(1)$[a] | | * | | |
| 130-200 | nitroethane | PbO | $CH_3CN$ | * | * | * | * |
| 150,190, 210 | nitroethane | | $N_2O$ | * | * | * | * |
| 150 | | | $CO_2(1)$[a] | * | * | * | * |
| 150 | | | $H_2O$ | | | * | |
| 150 | | | $N_2$ | | * | * | * |
| 130-200 | | | $H_3CCH=NOH$ | | * | | * |
| 150 | | | $C_2H_4$ (trace) | | * | | |
| 150 | | | $CH_4$ (trace) | | * | | |
| 150 | | | $C_4H_8(2)$[b] (trace) | | | | * |
| 150 | nitroethane | FeO(OH) | $CH_3CN$ | | * | | |
| 150 | | | $CO_2$ (1) | | * | | |
| 150 | | | $H_3CCH = NOH$ | * | | | |
| 190° | 1- nitropropane | PbO | $CH_3-CH_2-CN$ | | * | | * |
| 190° | 1- nitrobutane | PbO | $CH_3-CH_2-CH_2-CN$ | | * | | |
| 150°, 200° | 2--nitropropane | PbO | $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (50%) | * | * | * | * |
| | | | (trace) $C_6H_{12}$[c](3)(4-methyl -2-pentene) | | | | * |
| | | | $C_6H_{12}$[c] (3) | | | | * |
| | | | (trace) $C_3H_4$[d] (4) | | | | * |
| | | | $N_2O$ (20%) | * | | * | * |

Table 4 (continued)

| Reaction Temperature | Organic Reactant | Oxide | Products observed | Analytical Method Used | | | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | | | IR | GC | MS | GCMS |
| | | | $CO_2$ | | * | | * |
| | | (4) | $C_4H_8$ (trace) | | | | * |
| | | | $C_5H_{10}^d(4)$ trace | | | | * |
| | | | $H_2O$ | | | * | |
| 180 | acetaldoxime | PbO | $CH_3CN$ | | * | | * |
| 180° | 2-nitro-2-methylpropane | PbO | no reaction 24 hrs | | | | |
| 160 | acetone | PbO | no reaction (.5 hrs) | | | | |
| | 2,4-pentanedione | PbO | Acetone | | * | | |
| | | | 1 acetone/ 2,4-pentadione | | | | |
| 160 | acetone oxime | PbO | acetone | | * | | |
| 150 | nitroethane | $Fe_2O_3$ | No reaction 30 min. | | | | |
| 180 | " | SnO | " | " | | | |
| 150 | " | $ThO_2$ | " | " | | | |
| 150 | " | $MoO_3$ | " | " | | | |
| " | " | BaO | " | " | | | |
| " | " | CoO | " | " | | | |
| " | " | soda lime | " | " | | | |
| 150° | nitroethane | $PbO_2$ | $CO_2$ | | | * | |
| | | | $N_2$ | | | * | |
| | | | $H_2O$ | | | * | |
| | | | $Pb_3O_4$ }Visual inspection | | | | |
| | | | PbO } | | | | |

Table 4 (continued)

[a] $CO_2$ was present as $PbCO_3$ as indicated by IR, no free $CO_2$ was detected, identification was provided by acidification of solid and analysing the resultant gas.

[b] Isomer of $C_4H_g$ unknown, suspect 2 butene.

[c] Mass spectral data was insufficient to distinguish between the possible $C_6H_{12}$ isomers however the smaller of the two g.c. peaks with MN 34 had an identical retention time with cis or trans 4 methyl 2 pentene (these two isomers had identical retention times). The larger peak had a longer retention time than 4 methyl 2 pentene and is suspected to be 2, 3 dimethyl 2 butene.

[d] The mass spectral data was not sufficient to ascentain with certainty the specific isomer. It is possible that the $C_5H_{10}$, $C_4H_g$ species may arise from impurities, see below.

FIG. 1 ARRHENIUS PLOT FOR n-PROPYL NITRATE PYROLYSIS

$k = 10^{16.3} \exp{-40,200/RT}\ \text{SEC}^{-1}$
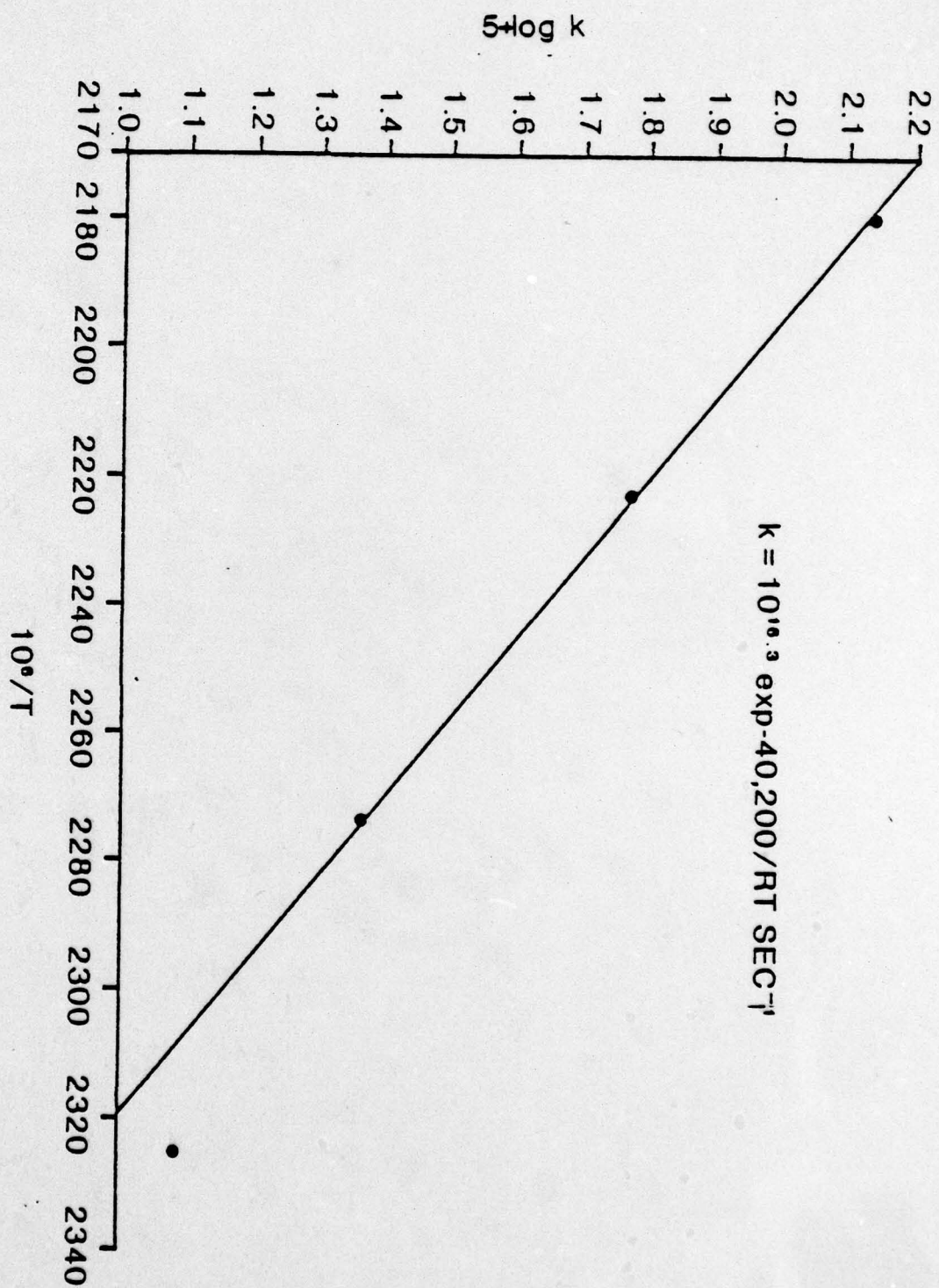
THE THERMAL DECOMPOSITION
OF NITROETHANE OVER
LEAD OXIDE AT 151°C

FIG. 2

FIG. 3



THE INDUCTION PERIOD
FOR THE NITROETHANE
-LEAD OXIDE SYSTEM

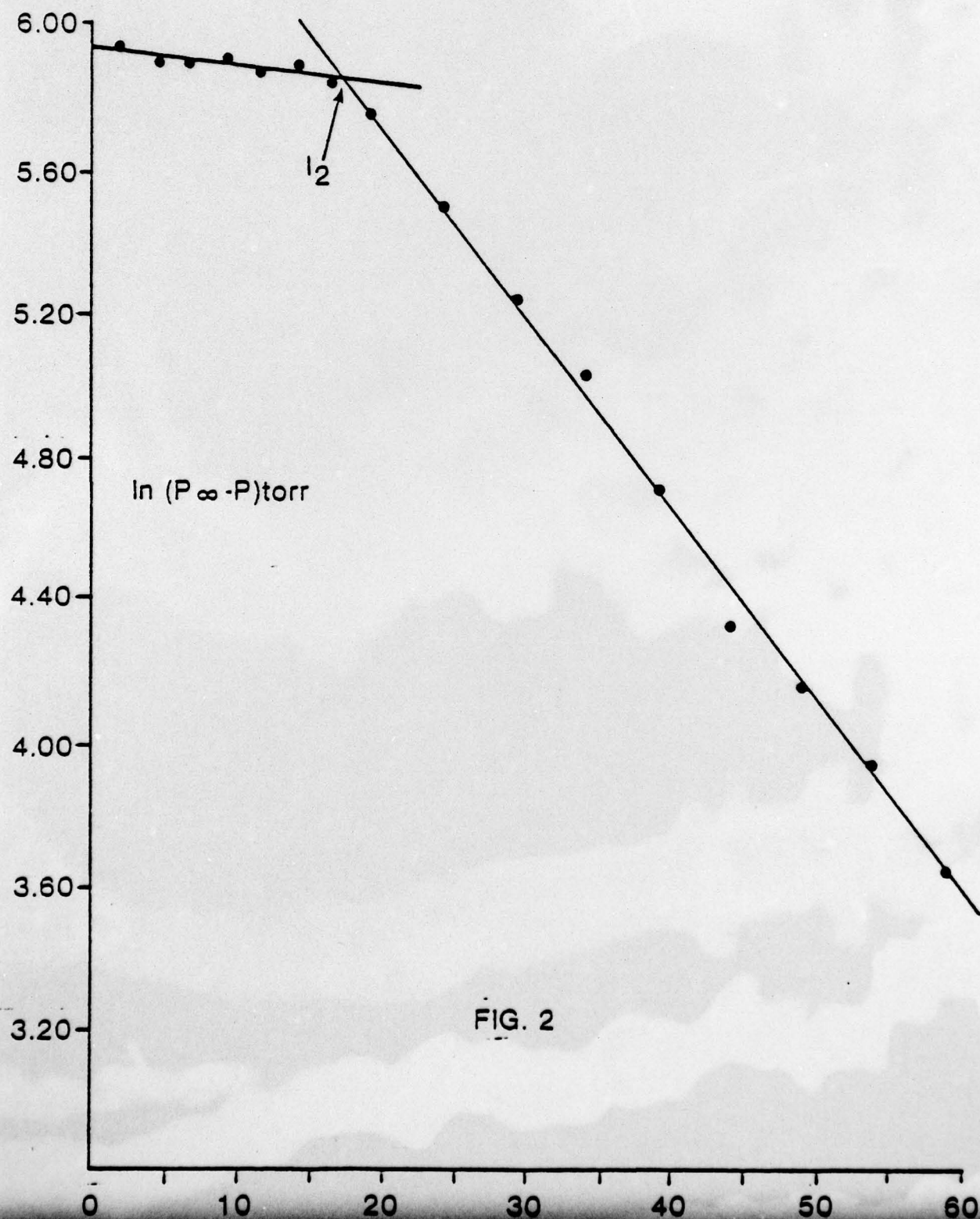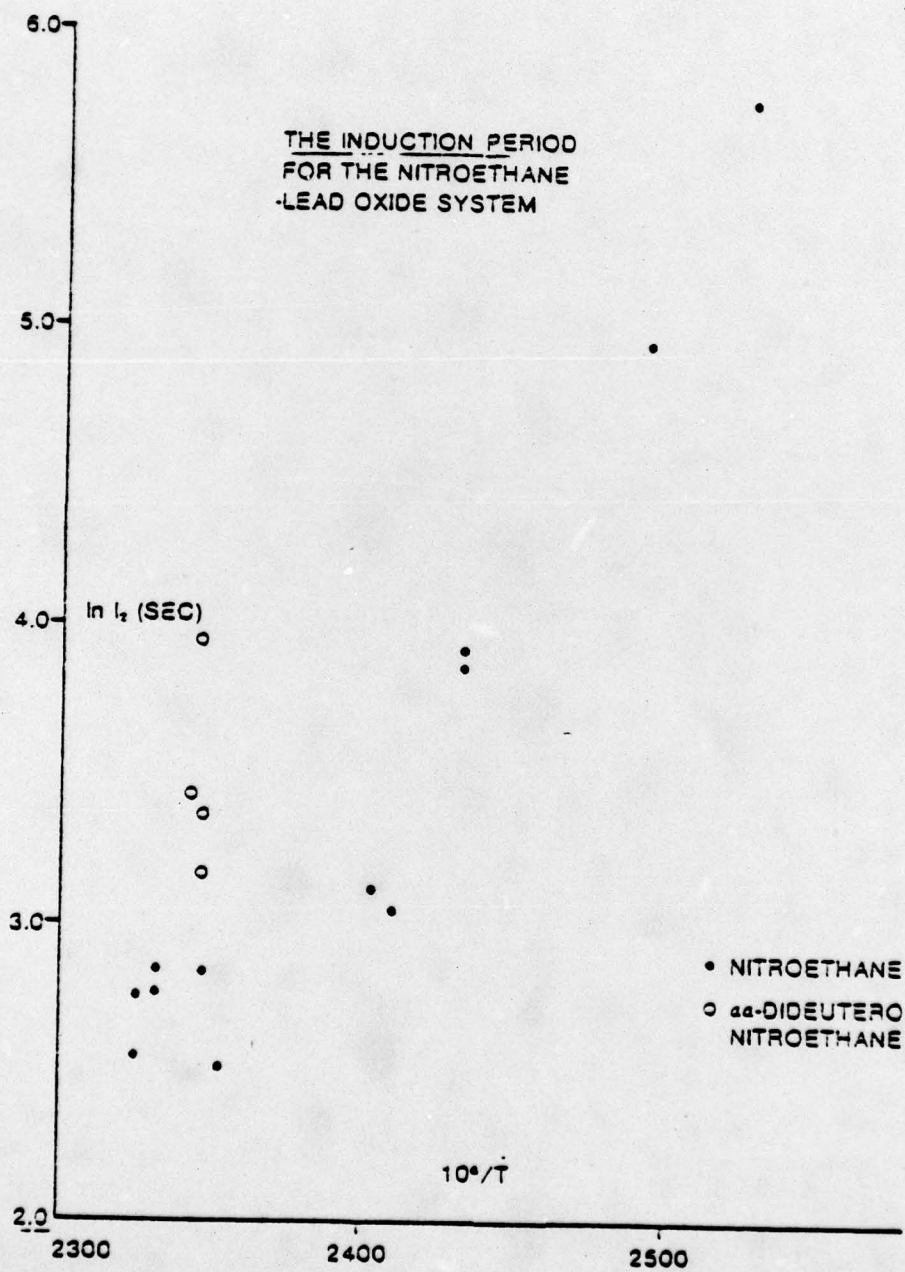$\ln I_z$ (SEC)

$10^6/T$

• NITROETHANE

○ $\alpha\alpha$-DIDEUTERO
NITROETHANE

REFERENCES

1. M. Kubota, T. J. Ohlemiller, L. H. Caveny and M. Summerfield, " The Mechanism of Super-rate Burning of Catalyzed Double Base Propellants", Aerospace and Mechanical Sciences Report No. 1087, Department of Aerospace and Mechanical Sciences, Princeton, N.J. , March (1973).

2. N. P. Suh, G. F. Adams and C. Lenchitz, "Observations on the Role of Lead Modifiers in Super-Rate Burning of Nitrocellulose Propellants", Combustion and Flame, 22, 289 (1974).

3. D. J. Hewkin, J. A. Hicks, J. Powling and J. Watts, "The Combustion of Nitric Ester-Based Propellants. Ballistics Modification by Lead Compounds", Comb. Sci. and Tech., 2, 307 (1971).

4. W. R. Ellis, B. M. Smythe and E.D. Trebarne, Fifth Symposium (International) on Combustion, Reinhold, New York, 1955 P. 641.

5. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", John Wiley and Sons, Inc., New York, 1962, pp. 715-716.

6. Feuer, H., Ed. "The Chemistry of Nitro and Nitroso Groups", Vol. I, Academic Press, New York, 1969, pp. 255-256.

7. Feuer, H., Ed. "The Chemistry of Nitro and Nitroso Groups", Vol. I, Academic Press, New York, 1969, pp 384-385.

8. Feuer, H., Ed. "The Chemistry of Nitro and Nitroso Groups", Vol. I, Academic Press, New York, 1969, p. 368.

9. Vogel, A. I., "A Textbook of Practical Organic Chemistry Including Qualitative Organic Analysis", Third Edition, John Wiley and Sons Inc., New York, N.Y., 1962.